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STRUCTURAL INTERPRETATION OF THE CONCENTRATION DEPENDENCES OF MOLAR VOLUME IN LEAD SILICATE GLASSES

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It is found that the type of the concentration dependence of molar volume in binary lead silicate glasses containing modifier oxides of groups I and II of the periodic system is determined by the degree of depolymerization of the structural lattice. The molar volume of the structural lattice of the considered glasses is additive and determined by the partial values of the molar volumes of their “siliceous” and “plumbate” components.

We earlier [1, 2] proposed a method for the structural interpretation of the concentration dependences of silicate glass properties (using the molar volume as example) based on establishing a correlation between the values of the selected property and the degree of depolymerization R^* of the silicon-oxygen frame (structural lattice) of the glass, which reflects the number of non-bridge oxygen ions per silicon-oxygen tetrahedron. The calculation error in determination of the molar volume using this method was, as a rule, about 1%.

According to the data in [1, 2], the molar volume of glass is calculated according to the equation which approximates the dependence of molar volume V_m on the depolymerization degree R^* of the structural lattice of glass:

$$V_m = V_{\text{Si}} + k_1 R^* + k_2 R^{*2}, \quad (1)$$

where $V_{\text{Si}} = 27.29 \text{ cm}^3/\text{mole}$ is the molar volume of vitreous silica calculated from its density, equal to 2.202 g/cm^3 ; $R^* = \frac{\sum x_j}{2(1 - \sum x_j)}$; $k_1 = \frac{\sum k_{1j} x_j}{\sum x_j}$; $k_2 = \frac{\sum k_{2j} x_j}{\sum x_j}$; k_{1j} and k_{2j} are the partial coefficients of the modifying oxides; x_j are the molar fractions of the modifying oxides.

The present study verified the applicability of the method described in [1, 2] for approximation of the concentration dependences of lead silicate glass properties.

Compared to silicate glasses containing modifier oxides of groups I and II of the Mendeleev periodic system of elements, lead silicate glasses have a wider region of glass formation.

System	Upper boundary of glass-forming region, R_xO molar content,* %
$\text{Li}_2\text{O} - \text{SiO}_2$	35.5
$\text{Na}_2\text{O} - \text{SiO}_2$	58.0
$\text{K}_2\text{O} - \text{SiO}_2$	54.5
$\text{Rb}_2\text{O} - \text{SiO}_2$	59.4
$\text{MgO} - \text{SiO}_2$	42.5
$\text{CaO} - \text{SiO}_2$	56.7
$\text{SrO} - \text{SiO}_2$	40.0
$\text{BaO} - \text{SiO}_2$	40.0
$\text{PbO} - \text{SiO}_2$	67.0

* Data from reference book [3].

This is determined by the high polarization capacity of the valence non-coupled electrons $6p^2$ in the Pb^{2+} ion, which are capable of forming directed, predominantly covalent bonds, for instance, with O^{2-} ions contained in $[\text{SiO}_4]$ tetrahedrons, which are the main structural elements of the glass-forming frame in silicate glasses.

It is known that Pb^{2+} ions in lead silicate glasses (as distinct from silicate glasses containing only modifying cations of groups I and II of the periodic system) are essentially not modifying cations in their traditional meaning, since their introduction to the glass composition does not lead to the formation of non-bridge oxygen ions, but is accompanied by the formation of “pseudo-bridge bonds” $-\text{O}-\text{Pb}-\text{O}-$ between the $[\text{SiO}_4]$ tetrahedrons in the glass structural lattice. The data in [4–9] suggest the possibility of the existence of such “pseudo-bridge bonds.”

The probability of this type of structural lattice in lead silicate glasses is further corroborated by the data on the structure of lead silicates formed in the $\text{PbO} - \text{SiO}_2$ system. The existence of the following compounds in this system has

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been established: $\text{PbO} \cdot \text{SiO}_2$, $3\text{PbO} \cdot 2\text{SiO}_2$, $2\text{PbO} \cdot \text{SiO}_2$, and $4\text{PbO} \cdot \text{SiO}_2$ [10].

The simplified schemes of possible coupling of $[\text{SiO}_4]$ tetrahedrons in the specified lead silicates constructed according to the data in [11, 12], neglecting the angles at which the tetrahedrons are oriented toward each other in actual structures, are represented in Fig. 1.

Lead metasilicate (alamosite) $\text{PbO} \cdot \text{SiO}_2$ correlates with the structural formula $6\text{Pb}_{1/2}[\text{SiO}_3]_3$. This silicate belongs to the group of silicates with ring silicon-oxygen anions of finite dimensions formed by metasilicate groups $[\text{SiO}_3]^{2-}$. The anion groups have a two-tier structure: the anion groups arranged in different planes are cross-linked by pseudo-bridge bonds $-\text{O}-\text{Pb}-\text{O}-$ created by Pb^{2+} ions 4 – 6, whereas the anion groups located in the same plane are joined by pseudo-bridge bonds formed by Pb^{2+} ions 1 – 3 (Fig. 1a).

Trilead disilicate (barisilite) $3\text{PbO} \cdot 2\text{SiO}_2$ correlated with the structural formula $6\text{Pb}_{1/2}[\text{Si}_2\text{O}_7]$. The anion groups of this silicate formed by diortho groups $[\text{Si}_2\text{O}_7]^{6-}$ have the double-tier structure as well. Cross-linking of anion groups positioned in different planes is implemented through pseudo-bridge bonds $-\text{O}-\text{Pb}-\text{O}-$ created by Pb^{2+} ions 5 and 6, and anion groups located in the same plane are joined by pseudo-bridge bonds formed by Pb^{2+} ions 1 – 4 (Fig. 1b).

Lead orthosilicate $2\text{PbO} \cdot \text{SiO}_2$ correlates with the structural formula $4\text{Pb}_{1/2}[\text{SiO}_4]$. The two-tier anion groups of this silicate formed by ortho groups $[\text{SiO}_4]^{4-}$. Cross-linking of anion groups positioned in different planes is implemented through pseudo-bridge bonds $-\text{O}-\text{Pb}-\text{O}-$ created by Pb^{2+} ions 4, and anion groups located in the same plane are joined by pseudo-bridge bonds formed by Pb^{2+} ions 1 – 3 (Fig. 1c).

Tetralead silicate $4\text{PbO} \cdot \text{SiO}_2$ correlates with the structural formula $\text{Pb}_4[\text{SiO}_4]\text{O}_{4/2}$. The two-tier structural patterns of this silicate formed by ortho groups $[\text{SiO}_4]^{4-}$ which are cross-linked to the adjacent ortho groups by pseudo-bridge bonds $-\text{Pb}-\text{O}-\text{Pb}-$ created by Pb^{2+} ions 1 – 4 (Fig. 1d).

The above schemes of the structural patterns of various lead silicates do not claim absolute certainty and are illustrative; however, they make it possible to demonstrate that the structural lattice of lead silicate glasses can have a high degree of cohesion even at $R^* > 1$, which ensures the possibility of producing lead silicate glasses with the molar content of PbO exceeding 66%.

We analyzed the dependence of molar volume on the degree of structural lattice depolymerization R^* for lead silicate glasses of systems $\text{PbO} - \text{SiO}_2$, $\text{R}_2\text{O} - \text{PbO} - \text{SiO}_2$ ($\text{R}_2\text{O}: \text{Na}_2\text{O}, \text{K}_2\text{O}, \text{Rb}_2\text{O}$), and $\text{BaO} - \text{PbO} - \text{SiO}_2$. For this purpose, the experimental data on the specified glasses densities published by different authors were used.

The molar volume was calculated based on the formula

$$V_m = \frac{M_m}{\rho} = \frac{\sum m_{m(i)} x_i}{\rho},$$

where M_m is the molar weight of glass, g/mole; ρ is the glass

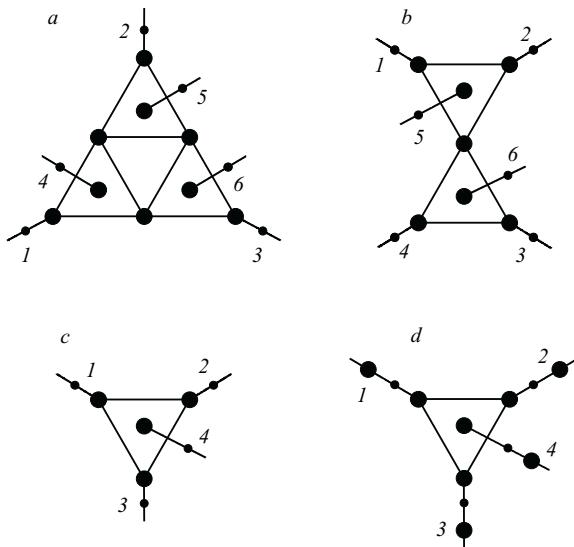


Fig. 1. Simplified patterns of possible coupling of $[\text{SiO}_4]$ tetrahedrons in the structure of various lead silicates: a) metasilicate; b) trilead disilicate; c) orthosilicate; d) tetralead silicates (Si^{4+} ions located in tetrahedron centers are not indicated in the figure); ● O^{2-} ; ● Pb^{2+} .

density, g/cm^3 ; $m_{m(i)}$ is the molar weights of oxides, g/mole; x_i is the molar fraction of oxides.

It was found that the dependence of the molar volume of the considered glasses on the degree of depolymerization R^* of their structural lattices can be approximated by an equation similar to equation (1):

$$V_m = V_{\text{Si}}(1 - x_{\text{Pb}}) + V_{\text{Pb}}x_{\text{Pb}} + k_1 R^* + k_2 R^{*2}, \quad (2)$$

where $V_{\text{Pb}} = 18.1 \text{ cm}^3/\text{mole}$ is the partial molar volume of PbO ; $R^* = \frac{x_j + x_{\text{Pb}}}{2(1 - x_j - x_{\text{Pb}})}$; $k_1 = \frac{k_{1j}x_j + k_{1\text{Pb}}x_{\text{Pb}}}{x_j + x_{\text{Pb}}}$; $k_2 = \frac{k_{2j}x_j + k_{2\text{Pb}}x_{\text{Pb}}}{x_j + x_{\text{Pb}}}$; x_{Pb} is the molar fraction of PbO .

The values of k_{1j} and k_{2j} are listed in Table 1; $k_{1\text{Pb}} = 1.7$, $k_{2\text{Pb}} = 0.7 \text{ cm}^3/\text{mole}$.

TABLE 1

Modifying oxide	k_{1j}^*	k_{2j}^*
Li_2O	-33.9	39.4
Na_2O	-17.7	22.6
K_2O	4.5	7.5
Rb_2O	21.4	-22.5
MgO	-29.0	18.6
CaO	-24.5	20.3
SrO	-22.3	22.0
BaO	-16.9	23.9

* Values of k_{1j} and k_{2j} are given based on the data in [1].

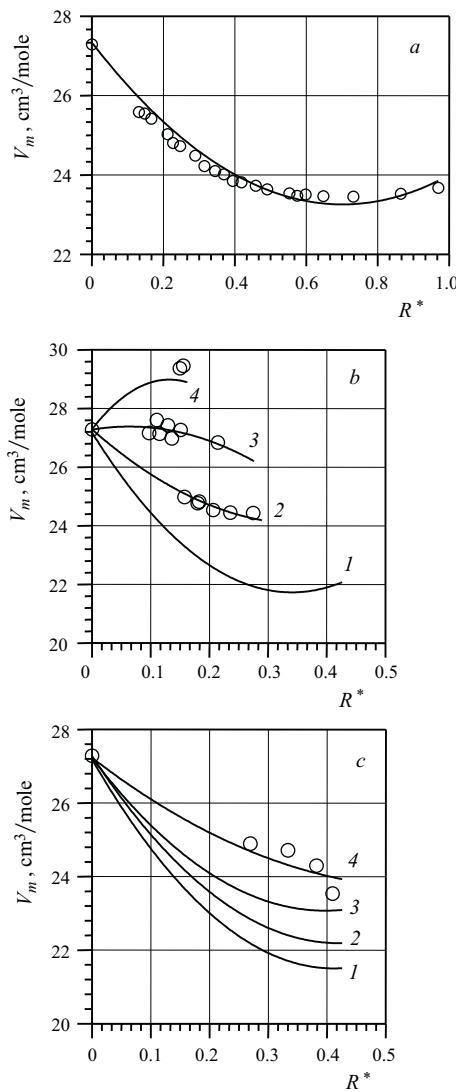


Fig. 2. Concentration dependences of molar volume V_m for glasses of systems $\text{PbO} - \text{SiO}_2$ (a), $\text{R}_2\text{O} - \text{PbO} - \text{SiO}_2$ (b), and $\text{RO} - \text{PbO} - \text{SiO}_2$ (c); R_2O , RO : Li_2O , MgO (1); Na_2O , CaO (2), K_2O , SrO (3); Rb_2O , BaO (4); solid lines) estimated values of V_m for glass compositions $c\text{R}_2\text{O} \cdot x\text{PbO} \cdot (1 - c - x)\text{SiO}_2$ and $c\text{RO} \cdot x\text{PbO} \cdot (1 - c - x)\text{SiO}_2$; for Li_2O and Na_2O $c = 0.24$; for K_2O $c = 0.14$; for Rb_2O $c = 0.17$; for RO $c = 0.21$; dots) experimental data by different authors (Table 2).

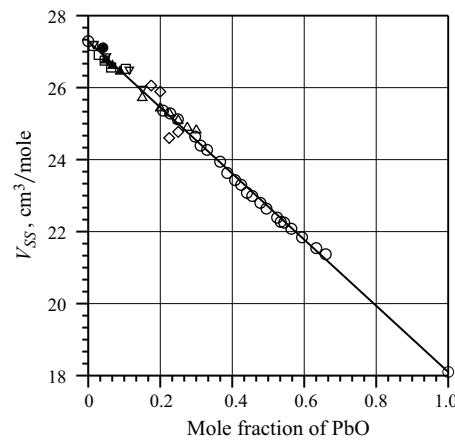


Fig. 3. Concentration dependences of the parameter V_{SS} for glass compositions: $x\text{PbO} \cdot (1 - x)\text{SiO}_2$, $c\text{R}_2\text{O} \cdot x\text{PbO} \cdot (1 - c - x)\text{SiO}_2$, and $c\text{RO} \cdot x\text{PbO} \cdot (1 - c - x)\text{SiO}_2$; \circ) PbO ; \square) $c = 0.23$ for Na_2O ; \triangle) $c = 0.05$; \blacktriangle) $c = 0.13$; \triangledown) $c = 0.19$ for K_2O ; \bullet) $c = 0.20$ for Rb_2O ; \diamond) $c = x$ for BaO ; solid lines) estimated values; dots) experimental data by different authors (Table 2).

The physical meaning of the factors $(1 - x_{\text{Pb}})$ and x_{Pb} in equation (2) is related to the content of the "siliceous" and "plumbate" components in the structural lattice of the glass.

The parameter R^* in equation (2) can be considered only conditionally as the degree of depolymerization of the structural lattice of glass, since the expression used for the calculation includes not only the molar fraction of the modifying oxides x_j which actually participate in the depolymerization of the silicon-oxygen glass frame, but the molar fraction of PbO as well, whose cation Pb^{2+} determines the formation of pseudo-bridge bonds $-\text{O}-\text{Pb}-\text{O}-$ in the frame. Accordingly, the physical meaning of the parameter R^* in equation (2) is the average total number of modifier cations of groups I and II of the periodic system and cations Pb^{2+} per silicon-oxygen tetrahedron.

The characteristics of the initial experimental data used in the analysis of the concentration dependences of the molar volume of the considered lead silicate glasses, as well as the mean quadratic error of V_m , are given in Table 2.

Thus, the obtained results indicate that the methods described in [1, 2] can be used to approximate the concentration dependences of properties of binary lead silicate glasses containing modifying oxides of groups I and II of the periodic system (Table 2 and Fig. 2).

Based on equation (2) it is possible to obtain the expression for the calculation of the molar volume of the structural lattice of glass:

$$V_{SS} = V_m - k_1 R^* - k_2 R^{*2} = V_{\text{Si}} (1 - x_{\text{Pb}}) + V_{\text{Pb}} x_{\text{Pb}}. \quad (3)$$

According to expression (3), V_{SS} of the binary lead silicate glasses, as well as lead silicate glasses containing modifying oxides of groups I and II of the periodic system, is additive and determined by the partial values of the molar vo-

TABLE 2

System	Relative mean quadratic error of V_m , %	Number of glass compositions used in data processing	Published source
$\text{Na}_2\text{O} - \text{PbO} - \text{SiO}_2$	0.54	10	[13]
$\text{K}_2\text{O} - \text{PbO} - \text{SiO}_2$	0.67	34	[13–15]
$\text{Rb}_2\text{O} - \text{PbO} - \text{SiO}_2$	1.37	2	[14]
$\text{BaO} - \text{PbO} - \text{SiO}_2$	1.65	7	[14, 15]
$\text{PbO} - \text{SiO}_2$	0.49	28	[3] [*]

* Glass composition is based on analysis.

lumes of the “siliceous” and “plumbate” components of the structural lattice (Fig. 3). Accordingly, the concentration dependence of the parameter V_{ss} should be approximated by the same linear function which should be true for the glasses of both considered series, which is substantiated by the obtained data.

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